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64 Polyethylene stabilizer compositions comprising compounds with piperidine groups and metal compounds.

A polyethylene stabilizer composition comprises:

A) one or more compounds with piperidine groups of the formula (I) or (Ia)

$$H_3^{C}$$
 CH_3
 R
 H_3^{C}
 CH_3
 H_3^{C}
 CH_3
 H_3^{C}
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

in which R is hydrogen, C₁-C₄-alkyl, allyl, benzyl, acetyl, acryloyl, 2-hydroxyethyl or 2-hydroxypropyl and

B) one or more metal compounds such as oxides and hydroxides of Al, Mg and Zn and, if appropriate, one or more salts of Al, Ba, Ca, Mg, Sr and Zn with C₁-C₂₂-carboxylic acids.

Description

Polyethylene stabilizer compositions comprising compounds with piperidine groups and metal compounds

The present invention relates to a novel method for stabilizing polyethylene against photooxidative degradation by using mixtures of 2,2,6,6-tetramethylpiperidine derivatives and particular metal compounds.

Polyethylene is here to be understood as meaning linear or branched polymers of ethylene of low, medium and high density, their mixtures in any proportions and also ethylene copolymers with aliphatic $C_3-C_{12}-\alpha$ -olefines containing up to 20% of di- α -olefine.

Of particular interest are branched low-density polyethylene, generally known as LDPE, and linear lowdensity polyethylene, generally designated as LLDPE, and their mixtures in any proportion.

It is known that polyethylene undergoes a progressive decrease in mechanical strength up to embrittlement when it is exposed to sunlight, as a result of photooxidative degradation caused by ultraviolet radiation.

To overcome this drawback it is necessary to add to the polymer suitable light stabilizers, for example certain derivatives of benzophenone and benzotriazole, nickel complexes, esters of substituted benzoic acids or sterically hindered amines.

Certain 2,2,6,6-tetramethylpiperidine derivatives of relatively high molecular weight have recently shown remarkable efficacy; nevertheless, the results obtained with these compounds have not been completely satisfactory, so that a further improvement was desirable.

It has now been found surprisingly that, when particular mixtures of one or more 2,2,6,6-tetramethylpiperidine derivatives with one or more metal compounds are used, light stability values are obtained which are significantly higher than those given by the use of piperidine compounds alone.

In particular, the present invention relates to a novel method for stabilizing polyethylene, which comprises the use of synergistic mixtures composed of

(A) one or more compounds with groups of the formula (I) or (Ia)

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$$H_3$$
C CH_3 H_3 C CH_3 CH_2 CH_2 CH_3 CH_3 CH_3

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in which R is hydrogen, C_1 - C_4 -alkyl, allyl, benzyl, acetyl, acryloyl, 2-hydroxyethyl or 2-hydroxypropyl, preferably hydrogen or methyl, and

(B) one or more metal compounds comprising oxides and hydroxides of Al, Mg and Zn, preferably Mg and Zn.

If appropriate, the following can be added to the mixtures of (A) + (B):

(C) one or more salts of Al, Ba, Ca, Mg, Sr and Zn with C₁-C₂₂-carboxylic acids, preferably the salts of Al, Ca, Mg or Zn with C₁₂-C₁₈-carboxylic acids. The use of certain 2,2,6,6-tetramethylpiperidine derivatives mixed with oxides or hydroxides of Mg or Zn as stabilizers for polymers was already known, but was restricted to the stabilization of polyurethanes.

In particular, Japanese Patent 82-34,155, published on 24.2.1982, claims the stabilization of polyurethanes with mixtures comprising esters of 2,2,6,6-tetramethyl-4-piperidinol, oxides or hydroxides of Mg or Zn and organic phosphites. The said mixtures do not give satisfactory results when used for stabilizing polyethylene.

On the other hand, British Patent 2,132,621 describes the use of mixtures of zinc oxide and esters of 2,2,6,6-tetramethyl-4-piperidinol as photodegrading agents for polyolefines, in particular polyethylene and polypropylene.

The synergistic stabilizing effect, obtained with the mixtures of the present invention, on polyethylene is therefore surprising.

Compounds (A) which contain the group of the formula (I) or (Ia) and can be used according to the present invention are:

(A1) The compounds claimed in US Patent 4,086,204, preferably those of the formula (II)

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in which R_1 is C_1 - C_8 -alkyl, cyclohexyl, 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, R_2 is hydrogen or C_1 - C_8 -alkyl, R_3 is hydrogen or methyl, R_4 is C_2 - C_6 -alkylene and n is a number from 2 to 20:

(A2) The compounds claimed in US Patent 4,104,248, preferably those of the formula (III)

in which R_1 is hydrogen or methyl, R_2 is \dot{C}_2 - C_6 -alkylene, R_3 is C_2 - C_6 -alkylene, 2-hydroxytrimethylene or xylylene and n is a number from 2 to 20:

(A3) The compounds claimed in US Patents 4,108,829 and 4,263,434, preferably those of the formula (IV)

$$\begin{bmatrix}
R_1 & R_2 & R_3 & R_2 & R_3 & R_4 & R_5 & R$$

in which R₁ is hydrogen or methyl, R₂ is hydrogen, C₁-C₈-alkyl, cyclohexyl, 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, n is 2, 3 or 4 and R₃ is the radical of an n-valent polyamine; (A4) The compounds claimed in US Patent 4,233,412, preferably those of the formula (V)

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in which R is C₂-C₈-alkylene and n is a number from 2 to 30; (A5) The compounds claimed in European Patent 22,080, preferably those of the formula (VI)

in which R_1 is hydrogen or methyl, n is 1 or 2, with $n=1\,\mathrm{X}$ is C_1 - C_{12} -alkyl, benzyl or -CH₂CH₂OH and Y is hydrogen or a group

and with n = 2 X is C_2 - C_6 -alkylene, xylylene or a group -(CH_2CH_2 - $\stackrel{N}{\gamma}$)_m CH_2CH_2 -,

where m is 1 or 2 and Z is a group of the formula

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and Y is hydrogen or a group

$$H_3C$$
 CH_3 $N-R_1$; H_3C CH_3

(A6) The compounds claimed in European Patent 29,522, preferably those of the formula (VII)

$$\begin{array}{c} X \\ X \\ X \\ X \\ \end{array}$$

$$\begin{array}{c} X \\ N \\ N \\ \end{array}$$

$$\begin{array}{c} X \\ N \\ \end{array}$$

$$\begin{array}{c} X \\ N \\ N \\ \end{array}$$

$$\begin{array}{c} X \\ N \\ N \\ \end{array}$$

$$\begin{array}{c} X \\ N \\ \end{array}$$

$$\begin{array}{c} X \\ N \\ N \\ \end{array}$$

$$\begin{array}{c} X \\ \\$$

in which I, m, n are 2 or 3, p and q are zero or 1 and X is a group

where R_1 is hydrogen or methyl, R_2 is C_2 - C_3 -alkylene and Y is OH, C_1 - C_8 -alkoxy, dimethylamino or diethylamino;

(A7) The compounds claimed in US Patent 4,288,593, preferably those of the formula (VIII)

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in which Q is a group of the formula

or a group of the formula

where R_1 is hydrogen or methyl and R_2 is C_1 - C_8 -alkyl; (A8) The compounds claimed in US Patent 4,315,859, preferably those of the formula (IX)

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in which R₁ is hydrogen or methyl, X is C₂-C₆-alkylene, A is -O-, -NH- or

m is 1 or 2, R2 is morpholino, hexamethyleneimino, -OR3 or

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where R_3 is C_1 - C_8 -alkyl allyl, cyclohexyl, phenyl or benzyl and R_4 and R_5 which can be identical or different are C_1 - C_8 -alkyl which may be interrupted by an oxygen atom, allyl, cyclohexyl, 2-hydroxyethyl, benzyl or a group

and R₅ can also be hydrogen;
(A9) The compounds claimed in US Patent 4,331,586, preferably those of the formula (X)

$$\begin{bmatrix} N & N & N & R_2 & N & CH_3 & H_3C & N & CH_3 & H_3C & R_1 & CH$$

in which R₁ is hydrogen or methyl, R₂ is C₂-C₆-alkylene and n is a number from 2 to 20;
(A10) The compounds claimed in European Patent 24,338, preferably those of the formula (XI)

in which R_1 is hydrogen or methyl, R_2 is C_2 - C_3 -alkylene, X is C_1 - C_8 -alkoxy, dimethylamino or diethylamino, R_3 is C_2 - C_6 -alkylene and n is a number from 2 to 20;

(A11) The compounds claimed in European Patent 42,554, preferably those of the formula (XII)

in which R_1 is C_1 - C_8 -alkyl; C_5 - C_9 -cycloalkyl, $(C_1$ - $C_4)$ -alkoxy propyl, dimethylaminopropyl or diethylaminopropyl, R_2 is C_2 - C_6 -alkylene and n is a number from 2 to 20;

(A12) The compounds claimed in European Patent 44,499, preferably those of the formula (XIII)

$$XNH-(CH_2)_n N N N (CH_2)_n-NHX$$

$$(CH_2)_n-NHX$$

$$(CH_2)_n-NHX$$

in which n is 2 or 3 and X is a group of the formula

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where R is hydrogen, C_1 - C_8 -alkyl, C_2 - C_4 -alkyl substituted by C_1 - C_4 -alkoxy or by di(C_1 - C_4 -alkyl)amino, or is cyclohexyl;

(A13) The compounds claimed in European Patent 70,386, preferably those of the formula (XIV)

in which R_1 is allyloxy, allylamino or diallylamino, R_2 is C_1 - C_4 -alkoxy, allyloxy, allylamino, diallylamino, C_1 - C_8 -dialkylamino, morpholino or a group

H₃C CH₃

N-R₃

R₅ H₃C CH₃

R₃ is hydrogen or methyl, R₅ is hydrogen, C₁-C₈-alkyl or a group

$$H_3^C$$
 H_3^C
 $H_3^$

and R4 is C2-C6-alkylene;

(A14) The polymers claimed in US Patents 4,413,093 and 4,435,555, obtained from compounds of the formula (XIV);

(A15) The compounds claimed in European Patent 72,009, preferably those of the formula (XV)

$$\begin{array}{c} H_{3}C \\ R_{1} \\ H_{3}C \\ \end{array} \begin{array}{c} CH_{2} \\ R_{2} \\ H_{3}C \\ \end{array} \begin{array}{c} CH_{2}CH_{2}OH \\ N \\ N \\ \end{array} \begin{array}{c} H_{3}C \\ N \\ N \\ \end{array} \begin{array}{c} CH_{3} \\ R_{2} \\ H_{3}C \\ \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ N \\ R_{2} \\ H_{3}C \\ \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ CH_{3}$$

in which R_1 is hydrogen or methyl, R_2 is hydrogen, C_1 - C_8 -alkyl, $(C_1$ - $C_4)$ -alkoxypropyl, dimethylaminopropyl, diethylaminopropyl, cyclohexyl or a group

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(A16) The compounds claimed in European Patent 75,849, preferably those of the formulae (XVI) and (XVII)

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$$(CH_2)_5$$
 $(CH_2)_5$ $(CH_2)_6$ $(CH_2)_5$ $(CH_2)_5$ $(CH_3)_6$ $(CH_2)_5$ $(CH_3)_6$ (CH_3)

in which R₁ is hydrogen or methyl, R₂ is hydrogen, C₁-C₈-alkyl, cyclohexyl, C₂-C₄-alkyl substituted by OH, C₁-C₄-alkoxy, dimethylamino or diethylamino, and n is a number from 2 to 6;

(A17) The compounds claimed in European Patent 82,244, preferably those of the formula (XVIII)

in which R_1 is allyloxy, allylamino or diallylamino, R_2 is the same as R_1 or is C_1 - C_8 -alkylamino, di(C_1 - C_4 -alkyl)amino, morpholino or a group

$$- \underset{R_3}{\overset{H_3C}{\longrightarrow}} \underset{H_3C}{\overset{CH_3}{\longrightarrow}}$$

R₃ is hydrogen, C₁-C₈-alkyl or a group

$$H_3C$$
 $N-R_4$
 H_3C
 CH_3
 R_4
 R_4

and R4 is hydrogen or methyl;

(A18) The compounds claimed in European Patent 94,048, preferably those of the formulae (XIX) and (XX)

in which n is a number from 1 to 10, R₁ is hydrogen or methyl, R₂ and R₃ which can be identical or different are C₁-C₈-alkyl or a group

$$H_3C$$
 CH_3
 H_3C
 CH_3
 GO

A₁ and A'₁ are hydrogen or a group

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and A₂ and A'₂ are a group

or A₂ is a group

and A'2 is a group

(A19) The compounds claimed in European Patent 107,615, preferably those of the formula (XXI)

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in which R_1 is C_1 - C_8 -alkyl, cyclohexyl, benzyl or C_2 - C_4 -alkyl substituted by C_1 - C_4 -alkoxy or dimethylamino or diethylamino, R_2 is hydrogen or methyl, X is morpholino or a group

-ORs or a group

where R_3 and R_4 which can be identical or different are C_1 - C_8 -alkyl, cyclohexyl, benzyl or C_2 - C_4 -alkyl substituted by OH, C_1 - C_4 -alkoxy, dimethylamino or diethylamino, R_4 can also be hydrogen and R_5 is C_1 - C_8 -alkyl, allyl, cyclohexyl or benzyl;

(A20) The compounds claimed in US Patent 4,477,615, preferably those of the formula (XXII)

in which m and n which can be identical or different are numbers from 2 to 6, p is a number from 2 to 20, R_1 is hydrogen or methyl, R_2 is hydrogen, C_1 - C_8 -alkyl, cyclohexyl or benzyl, R_3 is hydrogen or a group of the formula

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15 R₄ is C₂-C₆-alkylene, xylylene, 2-hydroxytrimethylene or a group of the formula

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where R₅ is C₁-C₈-alkoxy, phenoxy, C₁-C₈-alkylamino, di(C₁-C₄-alkyl)amino, cyclohexylamino, morpholino or a group

(A21) The compounds claimed in US Patent 4,533,688, preferably those of the formula (XXIII)

in which X is a group of the formula

where R₁ is hydrogen, C₁-C₈-alkyl, C₃-C₈-alkoxyalkyl, benzyl or a group

$$\begin{array}{c} H_3C \\ \hline \\ N-R_2 \\ H_3C \\ CH_3 \end{array}$$

R₂ is hydrogen or methyl and Y is hydrogen or a group

(A22) The compounds claimed in US Patent 4,540,728, preferably those of the formula (XXIV)

$$(CH_{2}=CH-CH_{2})_{2} = N$$

$$(CH_{2}=CH-CH_{2})_{2} = N$$

$$(CH_{3}=CH-CH_{2})_{2} = N$$

$$(CH_{3}=CH-CH_{3})_{3} = N$$

$$(N-R_{1}=CH_{3})_{3} = N$$

$$(XXIV)$$

$$(XXIV)$$

$$(XXIV)$$

in which R_1 is hydrogen or methyl and R_2 is hydrogen or C_1 - C_8 alkyl, and also the corresponding polymers of a molecular weight between 800 and 5,000;

(A23) The compounds claimed in European Patent 176,106, preferably those of the formula (XXV)

in which X is a group

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where R₁ is hydrogen or methyl and R₂ is hydrogen or C₁-C₈-alkyl.

Preferred compounds (A) are those of the formulae (II), (III), (IV), (V), (X) and (XXI).

Particularly preferred compounds (A) are those of the formula (II) in which R_1 is C_2 - C_8 -alkyl or cyclohexyl, R_2 is hydrogen or C_2 - C_8 -alkyl, R_3 is hydrogen or methyl, R_4 is -(CH_2)₂₋₆ and n is a number from 2 to 10, those of the formula (III) in which R_1 is hydrogen or methyl, R_2 is -(CH_2)₂₋₆, R_3 is -(CH_2)₂₋₆ and n is a number from 2 to 10, those of the formula (IV) in which R_1 is hydrogen or methyl, R_2 is C_1 - C_4 -alkyl, n is 2, 3 or 4 and R_3 is a group of the formula -NH(CH_2)₂₋₂-NH- for R_1 for R_2 -NH- (R_2)₂₋₃-NH- for R_3 -NH- for R_4

Compounds (A) of particular interest are:

The said compounds can be used by themselves or as a mixture with one another.

Compounds (B) which can be used according to the present invention ar preferably the oxides and hydroxides of Mg and Zn.

The oxid $\,$ s of $\,$ Mg and $\,$ Zn are particularly preferred, and they can be used by thems $\,$ lves or as a mixture with one another.

The compounds (C) which can be used according to the present invention, if desired, are preferably salts of Al, Ca, Mg and Zh with C₁₂-C₁₈-carboxylic acids.

The stearates of Ca, Mg and Zn, which can be used by themselves or as a mixture with one another, are particularly preferred.

The percentages by weight, relative to the weight of the polyethylene, of compounds (A), (B) and (C) are: 0.025 to 2%, preferably 0.05 to 1%, for compounds (A), 0.005 to 1%, preferably 0.025 to 0.5%, for compounds (B) and 0.005 to 1%, preferably 0.025 to 0.5%, for compounds (C).

The compounds (A), (B) and (C) can be mixed with one another before they are added to the polymer, or they can be added separately to the polymer, using any one of the known processes.

If desired, other additives conventional for polyethylene, such as phenolic antioxidants, phosphites, UV absorbers and other types of light stabilizers, can be added to the compounds (A), (B) and (C) of the present invention.

Examples of additives which can be mixed with the compounds (A) (B) and (C) are:

Phenolic antioxidants from the following classes:

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Alkylated monophenols, for example 2,6-di-t-butyl-4-methylphenol, 2-t-butyl-4,6-dimethylphenol, 2,6-di-t-butyl-4-ethylphenol, 2,6-di-t-butyl-4-n-butylphenol, 2,6-di-t-butyl-4-isobutylphenol, 2,6-di-cyclopentyl-4-methylphenol, 2-(α-methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricy-clohexylphenol, 2,6-di-t-butyl-4-methoxymethylphenol and 2,6-dinonyl-4-methylphenol.

Alkylated hydroquinones, for example 2,6-di-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,5-di-t-amylhydroquinone and 2,6-diphenyl-4-octadecyloxyphenol.

Thiobisphenols, for example 2,2'-thio-bis-(6-t-butyl-4-methylphenol), 2,2'-thio-bis-(4-octylphenol), 4,4'-thio-bis-(6-t-butyl-3-methylphenol) and 4,4'-thio-bis-(6-t-butyl-2-methylphenol).

Alkylidene-bisphenols, for example 2,2'-methylene-bis-(6-t-butyl-4-methylphenol), 2,2'-methylene-bis-(6-t-butyl-4-ethylphenol), 2,2'-methylene-bis-(4-methyl-6-(α -methylcyclohexyl)-phenol], 2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol), 2,2'-methylene-bis-(6-nonyl-4-methylphenol), 2,2'-methylene-bis-(4,6-di-t-butylphenol), 2,2'-ethylidene-bis-(6-t-butyl-4-isobutylphenol), 2,2'-ethylidene-bis-(6-t-butyl-4-isobutylphenol), 2,2'-methylene-bis-[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylene-bis-[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylene-bis-[6-(α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylene-bis-(6-t-butyl-2-methylphenol), 1,1-bis-(5-t-butyl-4-hydroxy-2-methylphenyl)-butane, 2,6-bis-(3-t-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris-(5-t-butyl-4-hydroxy-2-methylphenyl)-butane, 1,1-bis-(5-t-butyl-4-hydroxy-2-methylphenyl)-butane, 1,1-bis-(5-t-butyl-4-hydroxy-2-methylphenyl)-butane, bis-[2-(3'-t-butyl-4'-hydroxy-5'-methyl-benzyl)-6-t-butyl-4-methylphenyl] terephthalate.

Benzyl compounds, for example 1,3,5-tris-(3,5-di-t-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis-(3,5-di-t-butyl-4-hydroxybenzyl) sulfide, isooctyl 3,5-di-t-butyl-4-hydroxybenzylmercaptoacetate, bis-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) dithiolterephthalate, 1,3,5-tris-(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, dioctadecyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate, calcium monoethyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate and 1,3,5-tris-(3,5-dicy-clohexyl-4-hydroxybenzyl) isocyanurate.

Acylaminophenols, for example lauric acid 4-hydroxyanilide, stearic acid 4-hydroxyanilide, 2,4-bis-(octylmercapto)-6-(3,5-di-t-butyl-4-hydroxyanilino)-s-triazine and octyl N-(3,5-di-t-butyl-4-hydroxyphenyl)-carbamete

Esters of β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris-(hydroxyethyl) isocyanurate, thiodiethylene glycol and N,N'-bis-(hydroxyethyl)-oxamide.

Esters of β -(5-t-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols, for example methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris-(hydroxyethyl) isocyanurate, thiodiethylene glycol and N,N'-bis-(hydroxyethyl)-oxamide.

Esters of β-(3,5-dicyclohexyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris-(hydroxyethyl) isocyanurate, thiodiethylene glycol and N,N'-bis-(hydroxyethyl)-oxamide.

Amides of β -(3,5-di-t-butyl-4-hydroxyphenyl)-propionic acid, for example N,N'-bis-(3,5-di-t-butyl-4-hydroxyphenylpropionyl)-hexamethylenediamine, N,N'-bis-(3,5-di-t-butyl-4-hydroxyphenylpropionyl)-trim thylenediamine and N,N'-bis-(3,5-di-t-butyl-4-hydroxyphenylpropionyl)-hydrazine.

UV absorbers and light stabilizers

2-(2'-Hydroxyphenyl)-benzotriazoles, for example the 5'-methyl, 3',5'-di-t-butyl, 5'-t-butyl, 5'-(1,1,3,3-tetra-methylbutyl), 5-chloro-3',5'-di-t-butyl, 5-chloro-3',5'-di-t-butyl, 5'-t-butyl, 4'-octoxy-3',5'-di-t-amyl and 3',5'-bis-(α,α-dimethylbenzyl) derivatives.

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2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octoxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4.2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

Esters of various substituted benzoic acids, for example 4-t-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis-(4-t-butylbenzoyl)-resorcinol, benzoylresorcinol, 2,4-di-t-butylphenyl 3,5-di-t-butyl-4-hydroxybenzoate and hexad cyl 3,5-di-t-butyl-4-hydroxybenzoate.

Acrylates, for example ethyl α-cyano- β , β -diphenyl-acrylate, isooctyl α-cyano- β , β -diphenylacrylate, methyl α-carbomethoxycinnamate, methyl α-cyano- β -methyl-p-methoxycinnamate, butyl α-cyano- β -methyl-p-methoxycinnamate, butyl α-cyano- β -methyl-p-methoxycinnamate, methyl α-carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

Nickel compounds, for example nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-tetramethylbutyl)-phenol], such as the 1:1 or 1:2 complexes, which may contain additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of monoalkyl esters of 4-hydroxy-3,5-di-t-butylbenzylphosphonic acid, such as the methyl or ethyl esters, nickel complexes of ketoximes such as 2-hydroxy-4-methylphenyl undecyl ketoxime and nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypy-razole, with or without additional ligands.

Oxalic acid diamides, for example 4.4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-t-butyloxanilide, 2,2'-di-dodecyloxy-5,5'-di-t-butyloxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis-(3-dimethylaminopropyl)-oxamide, 2-ethoxy-5-t-butyl-2'-ethyloxanilide and its mixtures with 2-ethoxy-2'-ethyl-5,4'-di-t-butyloxanilide, and mixtures of ortho- and paramethoxy- and also o- and p-ethoxy-disubstituted oxanilides.

Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris-(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris-(2,4-di-t-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis-(2,4-di-t-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis-(2,4-di-t-butylphenyl) 4,4'-diphenylenediphosphonite and 3,9-bis-(2,4-di-t-butylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane.

The use of the stabilizer mixtures according to the present invention is illustrated by the examples which follow; these are given by way of illustration only and do not imply any restriction.

EXAMPLES 1 - 10

10 kg of low-density polyethylene powder of melt index 0.6 (Fertene EF 3-2000, a product from Soc. Enichem Polimeri) are mixed in a slow mixer with the compounds indicated in Table 1.

The mixtures are then extruded at a temperature of 190°C and converted into granules, from which stretched films of 150 um thickness are obtained by blow extrusion using a Dolci pilot extruder (screw diameter = 45/26 D and head diameter = 100 mm) under the following working conditions:

body temperature = 170-190-200°C head temperature = 200-200-200-190°C

The films obtained are exposed outdoors at 45°, facing south, on pinewood at Pontecchio Marconi (Bologna) (about 110 kly/year). The residual elongation is measured on samples, taken after various times of exposure by means of a constant-speed tensometer.

The energy received (expressed in kilolangleys) needed to halve the initial elongation value is then calculated (T_{50}).

The results obtained are shown in Table 1.

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TABLE 1

5	Example	Compound A		Compound B	Compound C	T50 elongation
	No.	, (g)		(g).	(g)	(kly)
	1	Compound	1	-	-	117
10		(20)				
70	2	11		MgO	_	168
				(10)		
15	3	11		Zn0	_	138
		•.		(10)		
	4	11		MgO	Ca stearate	193
20				(10)	(10)	
	5			Zn0	"	161
				(10)		
25	6	Compound	2	_	_	128
		(20).				
	7	11		MgO	-	175
30				(10)		
	8	11		ZnO ,	-	154
				(10)		
<i>35</i>	9	i,		MgO	Ca stearate	192
				(10)	(10)	
	10	1 11		Z nO	11	186
40				(10)		

Examples 11-18

10 kg of low-density polyethylene powder of melt index 0.1 (Fertene EF 3-2000, a product from Soc. ENICHEM POLIMERI) are mixed in a slow mixer with the compounds indicated in Table 2.

The mixtures are then extruded at a temperature of 190°C and converted into granules, from which stretched films of 150 µm thickness are obtained by blow extrusion using a Dolci pilot extruder (screw diameter = 45/26D and head diameter = 100 mm) under the following working conditions: body temperature = 170 - 190 - 200°C

head temperature = 200 - 200 - 200 - 190°C

The films obtained are exposed in a model 65 WR Weather - O -meter (ASTM G 26 - 77) with a black panel temperature of 63°C. The residual elongation is measured on samples, taken after various times of exposure to light, by means of a constant speed tensometer; the exposure time in hours (T_{50}) needed to halve the initial elongation value is then calculated. The results obtained are shown in Table 2:

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Table 2

Example N°	Compound A (g)	Compound B Compound C (g) (g)	T ₅₀ (hours)	5
11	compound 1	- <u>-</u>	3900 -	10
12		ZnO Ca stearate (5) (5)	> 4500	15
13	compound 3 (10)	- -	3600	20
14	н	ZnO Ca stearate (5) (5)	> 4500	25
15	compound 5 (10)	-	3140	25
16	11	ZnO Ca stearate (5) (5)	4100	30
17	compound 6 (10)	-	3040	35
18	11	ZnO Ca stearate (5) (5)	> 4500	40

Examples 19-21

10 kg of linear low-density polyethylene (LLDPE) powder of melt index 0.9 (Dowlex 2045, a product from Dow Chemical) are mixed in a slow mixer with 2 g of pentaerythritol-tetrakis [3-(3,5-di-t-butyl-4-hydroxy-phenyl)propionate], 8 g of tris-(2,4-di-t-butyl-phenyl)phosphite and with the compounds indicated in Table 3.

The mixtures are then extruded to give stretched films of 150 µm thickness by blow extrusion using a Dolci pilot extruder (screw diameter = 45/26D and head diameter = 100 mm) under the following working conditions:

body temperature: 180 - 220 - 220°C head temperature: 220 - 220 - 220 - 220°C

The films obtained are exposed outdoors at 45°, facing south, on pinewood at Pontecchio Marconi (Bologna) (about 110 kly/year). The residual elongation is measured on samples, taken after various times of exposure by means of a constant speed tensometer.

The energy received (xpress in Kilolangleys) n eded to halve the initial longation value is then calculated (T₅₀).

The results obtained are shown in Tabl 3.

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$$H_3^{C} \hookrightarrow H_3 \hookrightarrow H_9^{(n)} \hookrightarrow H_{3^{C} \hookrightarrow H_3} \hookrightarrow H_{3^{C} \hookrightarrow H_3}$$

13. A stabilizer composition according to claim 1, wherein the compound (A) is that of the formula

of a molecular weight between 2,000 and 4,000.

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ΔO

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14. A stabilizer composition according to claim 1, wherein the compound (A) is that of the formula

of a molecular weight between 2,000 and 4,000.

- 15. A stabilizer composition according to claim 1, wherein the compound (B) is an oxide or hydroxide of Mg or Zn.
- 16. A stabilizer composition according to claim 1, wherein the compound (B) is an oxide of Mg or Zn.
- 17 . A stabilizer composition according to claim 2, wherein the compound (C) is a salt of Al, Ca, Mg or Zn with C₁₂-C₁₈-carboxylic acid.
- 18. A stabilizer composition according to claim 2, wherein the compound (C) is a salt of Ca, Mg or Zn with stearic acid.
- 19. Stabilized polyethylene containing a stabilizer composition according to claim 1 or 2.
- 20. Stabilized polyethylene according to claim 19, wherein the percentages by weight, relative to the weight of the polyethylene, of compounds (A) and (B) are: 0.025 to 2%, preferably 0.05 to 1%, for compound (A) and 0.005 to 1%, preferably 0.025 to 0.5%, for compound (B).
- 21. Stabilized polyethylene according to claim 19, wherein the percentage by weight, relative to the polyethylene, of compound (C) is 0.005 to 1%, preferably 0.025 to 0.5%.
- 22. Stabilized polyethylene according to claim 19, which is low-density polyethylen (LDPE), linear low-d nsity polyethylene (LLDPE) or a mixture thereof.
- 23. A film, prepared from low-density polyethyl ne (LDPE), linear low-density polyethylene (LLDPE) or a mixtur thereof, stabilized with a stabilizer composition of claim 1 or 2.

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Polyethylene stabilizer compositions comprising compounds with piperidine groups and metal compounds.

A polyethylene stabilizer composition comprises:

 A) one or more compounds with piperidine groups of the formula (I) or (Ia)

in which R is hydrogen, C₁-C₄-aikyl, allyl, benzyl, acetyl, acryloyl, 2-hydroxyethyl or 2-hydroxypropyl and

B) one or more metal compounds such as oxides and hydroxides of Al, Mg and Zn and, if appropriate, one or more salts of Al, Ba, Ca, Mg, Sr and Zn with C₁-C₂₂-carboxylic acids.



EUROPEAN SEARCH REPORT

Application Number

EP 88 81 0267

	DOCUMENTS CONSID	ERED TO BE RELEVA	NT		
Category	Citation of document with indic of relevant passa	cation, where appropriate, ges	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)	
D,X	GB-A-2 132 621 (EXXO ENGINEERING CO.) * Claims *	N RESEARCH AND	1	C 08 K 5/34 C 08 K 3/22 C 08 L 23/02	
	PATENT ABSTRACTS OF 3 124 (C-416)[2571], 17 JP-A-61 261 332 (SUMI CO., LTD) 19-11-1986 * Abstract *	th April 1987; &			
				TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 08 K C 08 L	
	The present search report has be	en drawn up for all claims Date of completion of the sear	th.	Examiner	
T	HE HAGUE	28-11-1988	DE	. LOS ARCOS Y VELAZQU	
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same caregory A: technological background O: non-written disclosure P: intermediate document		E : earlier pat after the f ther D : document L : document & : member o	T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document		